

FIRE-RESISTANT AND WATER-RESISTANT HALOGEN-FREE
LOW-VOLTAGE CABLES

BACKGROUND OF THE INVENTION

Field of the invention

5 The present invention relates to electrical cables, in particular low-voltage electrical cables having improved fire resistance and water resistance.

Description of the prior art

10 Fire-resistant cables including polyolefin layers containing an organic halogenide or other fire retardants are known in the art.

15 The disadvantages of using halogenated flame retardant compounds, in particular in connection with fabrication of the above cables and their possible corrosive effect on metal parts of the equipment, are known in the art.

20 PCT WO 99/05688 discloses cables with good fire resistance properties, including a layer of crystalline propylene homopolymer or copolymer blended with a copolymer of ethylene with at least one α -olefin and possibly a diene.

 The above compounds contain a natural magnesium hydroxide in quantities which confer fire retardant properties on the cables.

25 The above application mentions the possible use of an internal insulative layer that is relatively thick compared with the layer containing the fire retardant.

30 European application EP 0 378 259 discloses high-voltage connecting cables including a metal wire surrounded by a first insulative layer from 0.3 to 1.5 mm thick and including a copolymer of propylene and at least one other alkene, the first insulative jacket being covered with a second insulative jacket that is not crosslinked and is from 1.0 to 3 mm thick, containing
35 polyvinyl chloride or a vinyl chloride copolymer. The

second jacket includes fire retardant additives.

GB patent 2 294 801 concerns an electrical cable including a conductor embedded in a hydrophobic material and surrounded by a layer of fire retardant material. The
5 cable is used in the field of telecommunications in particular.

However, we have found that using a covering including a layer containing the fire retardant as described in PCT WO 99/05688 makes the water resistance
10 of the cable unsatisfactory, failing to comply with the relevant requirements. Also, when the thick insulative additional layer is used, the cable has fire resistance problems.

We have found that when the cable is live in the
15 presence of moisture the water tends to penetrate the cable and reduce its insulation, leading to breakdown of the cable.

The invention therefore relates to a low-voltage electrical cable, preferably a single-conductor cable,
20 having improved fire resistance and flame propagation resistance, containing no halogenides and complying with IEC standards, the cable having improved water resistance. The combination also aims to improve the mechanical properties of the cable and its resistance to
25 short circuits.

The cable according to the invention must have a fire resistance complying with the following standards: IEC 332-3c (March 1992), NFEN 50 266-2 section 4 of February 1999, and NFC 32070 section 2 and 2.2 of March
30 1991, and the additions A1 of July 1992 and A2 of November 1993, and a water resistance such that it resists salt water (10 g/l NaCl) at 60°C at a voltage of 220 V DC for at least ten days, complying with NFC-32-201-2, art. 2.5 of October 1998 and NFC-32-201-1 table 3,
35 section 5 of October 1998.

We have discovered that the above problems can be solved by developing a cable featuring a double layer, the layers having relative thicknesses such that the cable has at one and the same time improved fire resistance properties and improved water resistance properties, in both cases complying with the aforementioned standards.

SUMMARY OF THE INVENTION

The invention provides a fire-resistant and water-resistant low-voltage electrical cable including a conductor and a first internal layer to protect it against water based on a polymer compound containing no halogen, crosslinked or not, and a second layer consisting of a blend of a crystalline propylene homopolymer or copolymer and of a copolymer of ethylene and at least one α -olefin, optionally with a diene, and of an agent having fire retardant properties, the ratio of the thicknesses of the outer layer and the internal layer being from 1 to 7.

Depending on the cross section of the conductor, the internal layer preferably has a thickness from 0.05 to 1 mm and the outer layer preferably has a thickness from 0.25 to 2 mm.

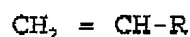
In accordance with the invention, the inner layer covering the conductor is a layer of an olefin polymer containing no halogenide, crosslinked or not, preferably chosen from polyolefins and more particularly olefin homopolymers or copolymers, copolymers of an olefin with ethylenically unsaturated esters, polyesters, polyethers, polyether/polyester copolymers and blends thereof.

The polymers can include polyethylene and in particular linear low-density polyethylene (LLDPE), polypropylene, a thermoplastic propylene-ethylene copolymer, ethylene-propylene rubbers (EPR) or ethylene-propylene-diene rubbers (EPDM), natural rubbers, butyl

rubbers, ethylene/vinyl acetate (EVA) copolymers, ethylene/methacrylate (EMA) copolymers, ethylene/ethyl acrylate (EEA) copolymers, ethylene/butyl acrylate (EBA) copolymers and ethylene/ α -olefin copolymers.

5 The fire retardant outer layer is preferably a blend of a crystalline propylene homopolymer or copolymer and of a copolymer of ethylene with an α -olefin, possibly with a diene, said copolymers having a narrow molecular weight distribution, characterized by a molecular weight
10 distribution index, defined as the ratio of the weight-average molecular weight M_w to the number-average molecular weight M_n , less than 5, preferably from 1.5 to 3.5, as determined by gel permeation chromatography and a fire retardant.

15 The α -olefins can be α -olefins with the formula:



where R is a linear or branched alkyl radical having from 1 to 10 carbon atoms.

In particular, they can be propylene, 1-butene,
20 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-dodecene, etc.

The α -olefins are preferably the propylene, 1-hexene and 1-octene radicals.

When the α -olefin is propylene, the copolymers can
25 be characterized by a high domain regularity in the sequence of monomer units. In particular, these copolymers have a number of CH_2 groups in the $-(\text{CH}_2)_n$ -sequences, where n is an integer, relative to the total number of CH_2 groups less than 5%/mol, preferably less
30 than 1%/mol. This can be determined by NMR analysis using carbon-13. This is known in the art.

When the comonomer is a diene, it generally has 4 to 20 carbon atoms and is preferably chosen from conjugated or unconjugated linear diolefins such as, for
35 example, 1,3-butadiene, 1,4-hexadiene or 1,6-octadiene;

monocyclic or polycyclic dienes such as, for example, 1,4-cyclohexadiene, 5-ethylidene norbornene, 5-methylene-2-norbornene, etc.

In accordance with the invention, the composition of the outer layer is obtained by using blends of the two polymers containing from 5 to 60 wt% and preferably from 10 to 40 wt% of a crystalline propylene homopolymer or copolymer (a) and from 40 to 95 wt% and preferably from 60 to 90 wt% of the ethylene/ α -olefin copolymer (b) relative to the total weight of the polymer components of the compound.

The compounds preferably contain, as fire retardants, natural or synthetic aluminum and/or magnesium hydroxide. The natural magnesium oxide can be obtained, for example, by grinding minerals based on magnesium hydroxide such as brucite. Brucite can generally be obtained mixed with other minerals such as calcite, aragonite, talc or magnesite, often in laminar form between silicate deposits, especially in serpentine asbestos, chlorites or schists.

In accordance with the invention, the brucite is ground employing a wet or dry technique known in the art and in the presence of additives such as polyglycols.

The specific surface area of the ground product is generally from 3 to 20 m²/g and preferably from 6 to 15 m²/g.

The ground product can be subjected to a separation process to obtain a range of particle sizes from 1 to 15 μ m and preferably from 1 to 5 μ m. The particle distribution is such that less than 10% of the total number of particles have a particle size less than 1.5 μ m and less than 10% of the total number of particles have a particle size greater than 20 μ m.

If the fire retardant is of natural origin, it may contain various impurities derived from oxides and/or

hydroxides of metals such as iron, manganese, calcium, silicon, vanadium, etc.

Magnesium hydroxide obtained by chemical methods known in the art can also be used, for example by basic
5 precipitation from an aqueous solution containing the Mg^{2+} ion.

The magnesium hydroxide can be used as such or can be treated with saturated or unsaturated fatty acids containing 8 to 24 carbon atoms or metal salts thereof,
10 for example with oleic acid, palmitic acid, stearic acid, isostearic acid, lauric acid, magnesium or zinc stearate, magnesium or zinc oleate.

The particles can also be surface-treated with coupling agents such as organic titanates or silanes,
15 such as vinyltriethoxysilane, vinyltriacetylsilane, tetraisopropyltitanate, tetra-n-butyl titanate, etc.

The copolymers (b) of the outer layer are preferably copolymers of ethylene with at least one C_3 - C_{12} α -olefin, possibly a diene, these copolymers having
20 elastomeric properties characterized by:

- an enthalpy of melting less than 35 J/g and preferably less than 30 J/g;

- an intrinsic viscosity (η) generally greater than 1.0 dl/g, and preferably greater than 2.0 dl/g,
25 determined in tetraline at 135°C;

- a Mooney ML (1+4) viscosity at 125°C, measured as per ASTM standard D 1646, generally greater than 10 and preferably from 20 to 90;

- a solubility in pentane at 20°C generally greater
30 than 80 wt%; and

- a permanent set of less than 30% measured one minute after removal of the stress, which allowed elongation to 200% as per ASTM standard D 412.

These copolymers generally have the following
35 composition: 35 to 90 mol% of ethylene 10 to 65 mol% of

α -olefin, preferably propylene, 0.10 mol% of a diene, preferably 1,4-hexadiene or 5-ethylidene norbornene.

When the α -olefin is propylene, the monomer composition is preferably as follows: 55 to 80 wt% and preferably 65 to 75 wt% of ethylene, 20 to 45 wt% and preferably 25 to 35 wt% of propylene; 0 to 10 wt% and preferably 0 to 5 wt% of a diene (preferably 5-ethylene-2-norbornene).

A second family of copolymers that can be used in the outer layer are copolymers of ethylene with at least one C_4 - C_{12} α -olefin, preferably 1-octene, and possibly a diene, characterized by:

- a density from 0.86 to 0.90 g/cm³;
- an enthalpy of melting from 30 to 60 J/g;
- a melt-flow index measured as per ASTM standard D 1238 L from 0.1 to 30 g/10 minutes, preferably from 0.5 to 5 g/10 minutes.

These copolymers preferably have the following composition: 75 to 97 mol% and preferably 90 to 95 mol% of ethylene; 3 to 25 mol% and preferably 5 to 10 mol% of α -olefin and 0 to 5 mol% and preferably 0.2 mol% of a diene.

The crystalline propylene homopolymers or copolymers generally have an enthalpy of melting greater than 75 J/g and preferably greater than 85 J/g. They are preferably chosen from:

- isotactic propylene homopolymers having an isotactic index greater than 80, preferably greater than 90 and in particular greater than 95;
- propylene homopolymers obtained using metallocene catalysts, having an mmmmm pentad concentration greater than 90% as determined by NMR analysis using carbon-13;
- copolymers of propylene with ethylene or an α -olefin having from 4 to 10 carbon atoms and an ethylene and/or α -olefin concentration less than 10 mol%;

- heterophase propylene copolymers which can be obtained by block polymerization of propylene and mixtures of propylene with ethylene and/or an α -olefin having 4 to 10 carbon atoms and containing at least
5 70 wt% of propylene homopolymers and crystalline ethylene/propylene copolymers with an isotactic index greater than 80, the remainder consisting of elastomeric ethylene/propylene copolymers with a propylene content from 30 to 70 wt%; and

10 - crystalline propylene homopolymers or copolymers having a syndiotactic structure that can be obtained using metallocene catalysts.

The quantity of magnesium hydroxide used as a fire retardant is finally from 10 to 90 wt% and preferably
15 from 30 to 80 wt% relative to the total weight of the compound.

Other fillers having flame retardant properties can be used, such as aluminum hydroxide or aluminum trihydrate ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) or one or more oxides or inorganic
20 salts such as CoO , TiO_2 , Sb_2O_3 , ZnO , Fe_2O_3 , CaCO_3 or mixtures thereof.

As indicated above, to improve the compatibility of the magnesium hydroxide with the polymer matrix, coupling agents can be used to improve the interaction between the
25 hydroxyl groups of the magnesium hydroxide and the polyolefin chains.

The coupling agents are preferably chosen from unsaturated silane derivatives, preferably silanes containing at least one ethylenically unsaturated group:
30 epoxides containing an ethylenically unsaturated group, monocarboxylic acids or preferably dicarboxylic acids having at least one ethylenically unsaturated group or derivatives thereof, such as anhydrides or esters.

The silanes include γ -methacryloxypropyl-
35 trimethoxysilane, methyltriethoxysilane, tris-(2-

methoxyethoxy)methylsilane, dimethyldiethoxysilane,
tris-(2-methoxyethoxy)vinylsilane, vinyltrimethoxy-
silane, vinyltriethoxysilane, octyltriethoxysilane,
isobutyltriethoxysilane, isobutyltrimethoxysilane and
5 mixtures thereof.

The epoxides include glycidyl acrylates, glycidyl
methacrylate, the monoglycidyl ester of itaconic acid,
the glycidyl ester of maleic acid, vinyl glycidyl ether,
allyl glycidyl ether or mixtures thereof.

10 The monocarboxylic or dicarboxylic acids including
an ethylenically unsaturated group include maleic acid,
maleic anhydride, fumaric acid, citraconic acid, itaconic
acid, acrylic acid, methacrylic acid, their esters and
anhydrides or mixtures thereof, maleic anhydride being
15 preferred.

The coupling agent is generally used in quantities
from 0.01 to 5 wt% and preferably 0.05 to 2 wt% relative
to the total weight of the base polymer blend.

20 These compounds can also contain antioxidants,
processing aids, lubricants, pigments and other fillers.

The compounds are prepared by mixing the polymers
and the additives by methods known in the art.

The layers can be applied by extrusion, for
example, or by extrusion in two separate stages,
25 consisting in extruding the inner layer onto the
conductor in a first stage and the outer layer onto the
inner layer in a second stage.

In a preferred embodiment the two layers are
applied in a single stage using a so-called "tandem"
30 process in which two separate extruders in series are
used or by coextrusion using a single extrusion head.

Cables according to the invention are intended in
particular to be used in environments where there are
moisture problems or places for which there are special
35 safety conditions in the event of fire, such as public

places, storage areas, test areas or working areas likely to receive inflammable products. They have improved short-circuit resistance.

The following examples are intended to illustrate the invention without limiting it.

The following composition was prepared:

Table I

	Composition	Weight %
10	Engage 8003	20.9
	Moplen EP1X35 F	3.7
	Hydrofy G. 1.5 S	73.3
	Irganox MD 1024	0.074
15	Irganox 1010	0.20
	Stearic acid	0.37
	VTMOEO silane	0.74
	Peroximon DC	0.074

20 The cable had a cross section of 1.5 mm² and a nominal total insulation thickness of 0.7 mm.

Table II

	Sample	A	B	C
25	Composition (Table I)	0.7	0.5	0.2
	(outer layer - mm)			
	Escorene LL 1004	0	0.2	0.5
30	(inner layer - mm)			
	Tensile strength (MPa)*	12.2	14.2	17.6
	Elongation at break (%)**	110	170	210

35

	Aging in salt water** (10 days) (NF-C 32-201-2)	no	yes	yes
5	Fire propagation test (IEC 332.3C of March 1992)	yes	yes	no
	Elongation at break	no	yes	yes
	Stress at break	no	yes	yes

10

* As per standard NF-C 32-201-1, table 1 section 1.1 column 6, October 1998.

** As per standard NF-C 32-201-2, art. 2-5, October 1998 and NF-C 32-201-1, table 3 section 5, October 1998.

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Examples A and C are comparative.

Engage 8003 is an ethylene/1-octene copolymer obtained by metallocene catalysis.

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The ratio by weight of ethylene/1-octene was equal to 82/18 (5.5 mol% of 1-octene, density = 0.885 g/cm³; MFI = 1.0 g/10 minutes; CDI > 70%; ΔH_{2m} = 55.6 J/g).

Moplen (EP1X35 HF) is a crystalline propylene/ethylene copolymer (d = 0.900 g/cm³; MFI = 9.0 g/10 minutes; T_m = 154°C; ΔH_{2m} = 90.6 J/g).

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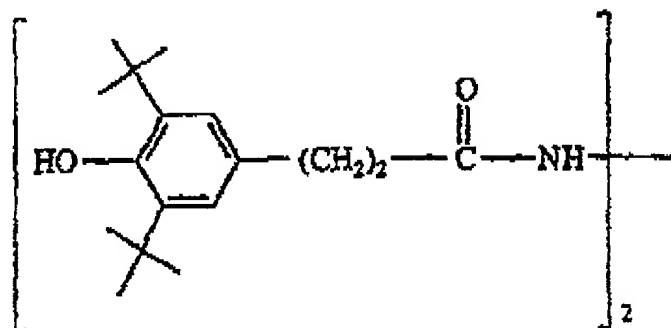
Hydrofy G 1.5 S is a magnesium hydroxide from SIMA surface-treated with stearic acid and has an aqueous extract conductivity of 290 μS/cm, a specific surface area of 10.4 m²/g; and a particle size distribution expressed in μm of:

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Table III			
	10%	50%	80%
	0.7	2.1	6.4
	(average)		

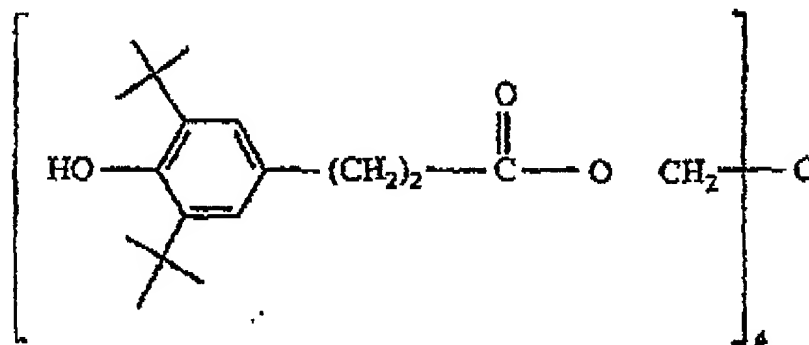
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Irganox MD 1024 is an antioxidant from CIBA with the formula:



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Irganox 1010 is an antioxidant from CIBA having the formula:



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VTMOEO silane is tris-(2-methoxyethoxy)vinylsilane with the formula $\text{CH}_2=\text{CH}-\text{Si}(\text{OCH}_2\text{H}_4\text{OCH}_3)_3$, with a purity of not less than 99 wt%.

Peroximon DC is dicumyl peroxide with a purity of not less than 99 wt% and the following formula:

